One or more embodiments relates to an MCrAlY bond coat comprising an MCrAlY layer in contact with a Y—Al2O3 layer. The MCrAlY layer is comprised of a γ—M solid solution, a β—MAl intermetallic phase, and Y-type intermetallics. The Y—Al2O3 layer is comprised of Yttrium atoms coordinated with oxygen atoms comprising the Al2O3 lattice. Both the MCrAlY layer and the Y—Al2O3 layer have a substantial absence of Y—Al oxides, providing advantage in the maintainability of the Yttrium reservoir within the MCrAlY bulk. The MCrAlY bond coat may be fabricated through application of a Y2O3 paste to an MCrAlY material, followed by heating in a non-oxidizing environment.

18 Claims, 2 Drawing Sheets
References Cited

OTHER PUBLICATIONS


* cited by examiner
MCRAIY BOND COAT WITH ENHANCED YTRIUM LAYER

RELATION TO OTHER APPLICATIONS

This patent application is a division of and claims priority from non-provisional patent application 13/363,486 filed Feb. 1, 2012, which is hereby incorporated by reference.

GOVERNMENT INTERESTS

The United States Government has rights in this invention pursuant to the employer-employee relationship of the Government to the inventors as U.S. Department of Energy employees and site-support contractors at the National Energy Technology Laboratory.

FIELD OF THE INVENTION

One or more embodiments relate to an MCRAIY bond coat comprised an MCRAIY layer in contact with a Y—Al₂O₃ layer. The MCRAIY composition is comprised of Yttrium and Aluminum, and further comprised of greater than 50 weight percent (wt. %) of a metal M, where the metal M is Ni, Co, Fe, or combinations thereof; and the MCRAIY layer is comprised of a γ-η solid solution, a β-MAI intermetallic phase, and Y-type intermetallics. The Y—Al₂O₃ layer is comprised of Yttrium atoms coordinated with oxygen atoms comprising the Al₂O₃ lattice. Both the MCRAIY layer and the Y—Al₂O₃ layer have a substantial absence of Y—Al oxides, providing advantage in the maintainability of the Yttrium reservoir within the MCRAIY bulk. A method of fabrication is additionally disclosed.

BACKGROUND

MCRAIY type coatings are commonly used as overlay coatings and bondcoats for the protection of components against high-temperature oxidation and corrosion. During exposure to high temperatures, an oxide scale forms on the MCRAIY surface, becoming part of the original system. This thermally grown oxide is largely comprised of alumina and often represents the starting point for failure. Correspondingly, the growth rate and adhesion of the oxide scale and the aluminum depletion in the bondcoat are among the determining factors for the useful lifetime of an MCRAIY bond coated article.

At long term exposures, the alumina scales are prone to spallation. The scale spallation is a common event under temperature cycling conditions due to the thermal expansion mismatch between the oxide and the metallic substrate, and failure is generally related to scale thickness, growth rate and adherence. The two latter parameters are crucially affected by the addition of Yttrium, as well as other reactive elements such as Lanthanum, Zirconium, and Hafnium. These reactive elements will commonly constitute some percentage, typically less than 0.5 wt. % to the base MCRAI composition. These reactive elements have been found to greatly improve alumina scale adherence and significantly increase the critical scale thickness for spallation. However, this beneficial effect is highly sensitive to the Y-concentration. In some cases, optimum oxidation and improved adherence is obtained by low concentrations of Y in the coating (around 0.1 wt. %), whereas a few tens of a weight percent more (over 0.5 wt. %) can lead to accelerated oxidation and detrimental oxide morphology. This implies that relatively low amounts of Yttrium are desired in the coating. Issues have arisen as a result of this Yttrium content sensitivity however, because Yttrium can be tied up by Y—Al oxides resulting from typical fabrication processes, and the effective Yttrium concentration of the MCRAIY coating may significantly deviate from that of the original MCRAIY source material.

Depletion of the Yttrium reservoir through the formation of excessive Y—Al oxides will therefore promote TGO spallation in service. Such depletion results in deviation from the optimum Yttrium content designed to obtain a compromise between the beneficial effect on oxide adherence without extensively enhancing the growth rate of the oxide. Defining and maintaining this optimum yttrium content it is absolutely necessary to take into account the actual Yttrium reservoir in the MCRAIY coating. See e.g., Toscano et al., “Parameters affecting TGO growth and adherence on MCRAIY-bond coats for TBC’s,” Surface & Coatings Technology 201 (2006), among others. It would be advantageous to provide an MCRAIY bond coat wherein the formation of Y—Al oxides is suppressed, and the Yttrium reservoir of the final heat treated composition could be largely defined by the Yttrium concentration of the original MCRAIY source material. Such an MCRAIY bond coat would mitigate variations in the Y-distribution and the reservoir of metallic Y in MCRAIY coatings and avoid the significant variations in the alumina scale growth rate and adherence which accrue from nominally equivalent MCRAIY bond coat compositions.

Additionally, a common feature of the oxide morphology in MCRAIY bond coats is the formation of Y₂O₃ compounds near or at the metal/oxide interface, known as pegs. The coefficient of diffusion of oxygen in Y₂O₃ is about 2.2×10⁻¹¹ cm²/s, and is considerably higher than the surrounding Al₂O₃, where the value is generally around 1x10⁻¹⁷ cm²/s (at 700°C). As a result, the presence of Y₂O₃ in the alumina scale is associated with locally accelerated oxidation along these Y-compounds, which leads to internal oxidations intruding in the coating alloy. In real oxide scales, this short-circuit path diffusion significantly impacts the kinetics of internal MCRAIY bulk oxidation. It would be additionally advantageous to provide an MCRAIY bond coat wherein an upper surface layer of Y—Al₂O₃ with an absence of Y₂O₃ could be formed, in order to mitigate internal MCRAIY bulk oxidations enabled by short-circuit path diffusion through Y₂O₃ in the upper layer. Such an absence of Y₂O₃ and other Y—Al oxides in the MCRAIY upper layer would further preserve the reservoir of metallic Y in MCRAIY coatings and promote MCRAIY effective lifetimes.

Provided here is an MCRAIY bond coat comprised of an MCRAIY layer in contact with a Y—Al₂O₃ layer. The MCRAIY layer is comprised of a γ-η solid solution, a β-MAI intermetallic phase, and Y-type intermetallics. The Y—Al₂O₃ layer is comprised of Yttrium atoms coordinated with oxygen atoms comprising the Al₂O₃ lattice. The MCRAIY layer and the Y—Al₂O₃ layer have a substantial absence of Y—Al oxides. The absence of selected Y—Al oxides within the MCRAIY layer provides advantage in the maintainability of the Yttrium reservoir within the MCRAIY bulk, and the absence of selected Y—Al oxides within the Y—Al₂O₃ layer mitigates oxygen diffusion and undesired modification of the originally intended Yttrium distribution in the underlying MCRAIY bulk.

These and other objects, aspects, and advantages of the present disclosure will become better understood with reference to the accompanying description and claims.

SUMMARY

The disclosure provides a bond coat comprised of an MCRAIY layer in contact with a Y—Al₂O₃ layer. The
MCrAIY may be further in contact with a substrate surface. The MCrAIY layer is comprised of Yttrium and Aluminum, and further comprised of greater than 50 weight percent (wt. %) of a metal M, where the metal M is Ni, Co, Fe, or combinations thereof. In an embodiment, the MCrAIY layer is in contact with a nickel-based substrate, and the metal M is Ni, Co, or Ni and Co. The MCrAIY layer is comprised of a γ-M solid solution, a β-MAl intermetallic phase, and Y-type intermetallics, and has a substantial absence of Yttrium-Aluminum Garnet (YAG) and Yttrium-Aluminum Perovskite (YAP) phases. The Y—Al₂O₃ layer is comprised of Yttrium atoms and Al₂O₃, where the Yttrium atoms are coordinated with oxygen atoms comprising the Al₂O₃ lattice. Generally, the Y—Al₂O₃ layer is comprised of equixed grains of Al₂O₃, where the Al₂O₃ grain boundaries are enriched with Yttrium at grain-boundary cation sites.

Additionally, the MCrAIY layer and Y—Al₂O₃ layer have a substantial absence of various Y—Al oxide phases, as opposed to typical MCrAIY bond coats generated through the vacuum heat treatment of MCrAIY materials. The absence of these Y—Al oxides maintains the Y-oxide distribution within the MCrAIY bulk and has a significant effect on the growth rate and adherence of the alumina scale and lifetime of the bond coat. The absence of these Y—Al oxides within the MCrAIY layer and the Y—Al₂O₃ layer is both advantageous and difficult to achieve.

In a particular embodiment, MCrAIY layer 101 and Y—Al₂O₃ layer 102 are fabricated by a process of depositing an MCrAIY material on a substrate, preparing a Y₂O₃ paste comprised of a halide activator, and heat treating the article in a non-oxidizing atmosphere to generate the MCrAIY layer and the Y—Al₂O₃ layer. The Y₂O₃ paste is comprised of Y₂O₃ and a halide activator, and may be further comprised of inert filler and inert transport fluid. The halide activator may be selected from any of the activators known for use in the pack cementation technique and suitable for the production of yttrium-containing vapors when placed in the presence of Y₂O₃ at sufficient temperature. The Y₂O₃, halide activator and optionally, inert filler, are combined and thoroughly mixed as required to make the Y₂O₃ paste composition. The Y₂O₃ paste is applied to the MCrAIY upper surface by any convenient, cost effective manner, and the paste covered article is heated in a non-oxidizing atmosphere at a temperature of from about 400°C to about 1300°C. For a sufficient period of time sufficient to generate the MCrAIY layer and the Y—Al₂O₃ layer. Following the heating period, any excess remaining Y₂O₃ paste may be removed from the heat treated article, generating a bond coated article.

The novel process and principles of operation are further discussed in the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates an embodiment of a bond coated article comprised of the MCrAIY layer and the Y—Al₂O₃ layer. FIG. 2 illustrates a second embodiment of a bond coated article comprised of the MCrAIY layer and the Y—Al₂O₃ layer. FIG. 3 illustrates an embodiment of a paste covered article comprised of an MCrAIY material and a Y₂O₃ paste.

DETAILED DESCRIPTION

The following description is provided to enable any person skilled in the art to use the invention and sets forth the best mode contemplated by the inventor for carrying out the invention. Various modifications, however, will remain readily apparent to those skilled in the art, since the principles of the present invention are defined herein specifically to provide a bond coated article comprised of a Y—Al₂O₃ layer atop an MCrAIY layer, where the Y—Al₂O₃ layer and the MCrAIY layer have a substantial absence of Yttrium-Aluminum Garnet and Yttrium-Aluminum Perovskite phases.

The disclosure provides a bond coat comprised of an MCrAIY layer in contact with a Y—Al₂O₃ layer. The MCrAIY layer may be further in contact with a substrate surface. The MCrAIY layer is comprised of Yttrium and Aluminum, and further comprised of greater than 50 weight percent (wt. %) of a metal M, where the metal M is Ni, Co, Fe, or combinations thereof. In an embodiment, the MCrAIY layer is in contact with a nickel-based substrate, and the metal M is Ni, Co, or Ni and Co. The MCrAIY layer is comprised of a γ-M solid solution, a β-MAl intermetallic phase, and Y-type intermetallics, and has a substantial absence of Yttrium-Aluminum Garnet (YAG) and Yttrium-Aluminum Perovskite (YAP) phases. The absence of YAG and YAP phases provides advantages in Y-distribution and maintainability of the Yttrium reservoir within the MCrAIY bulk over typical MCrAIY bond coats generated through the vacuum heat treatments.

The Y—Al₂O₃ layer is comprised of Yttrium atoms and Al₂O₃, where the Yttrium atoms are coordinated with oxygen atoms comprising the Al₂O₃ lattice. The Yttrium enrichment along the grain boundaries provides significant benefit in terms of oxygen diffusivity. Additionally, the Y—Al₂O₃ layer has a substantial absence of Yttria, YAG, and YAP phases, as opposed to the typical upper layers generated through the vacuum heat treatment of MCrAIY materials. The absence of Yttria and mixed Y—Al oxide compounds in the Y—Al₂O₃ layer mitigates diffusion and undesired modification of the originally intended Yttrium distribution in the underlying MCrAIY bulk. The absence of Yttria and mixed Y—Al oxide compounds additionally reduces scale spallation due to stress concentration and thermal expansion mismatch.

Within this disclosure, the descriptive “MCrAIY” when applied to a layer or material denotes a material composition comprised of a base metal M, chromium (Cr), aluminum (Al), and yttrium (Y), where the base metal M is typically Iron (Fe), Nickel (Ni), Cobalt (Co), or a combination of Ni and Co, and where the material composition is at least 50 wt. % of the base metal M, at least 10 wt. % Cr, and at least 7 wt. % Al, where the wt. % values are based on the total weight of the material composition. In an embodiment, the material composition is about 0.5 to about 1.5 wt. % yttrium. In a further embodiment, an MCrAIY material has a composition of 22 wt. % Cr, 10 wt. % Al, 1.0 wt. % Y, balance Ni. In another embodiment, an MCrAIY material has a composition of 52 wt. % Ni, 21 wt. % Cr, 8 wt. % Al, 0.5 wt. % Y, balance Co.

Within this disclosure, an “MCrAIY layer” means a layer having an MCrAIY composition and comprised of an γ-M solid solution, a β-MAl intermetallic phase, and Y-type intermetallics. A “γ-M solid solution” means a face-centered cubic (FCC) solid solution of the base metal M in the MCrAIY composition, where the base metal M is the solvent and Al, Cr, and possibly other elements, are the solute. “β-MAl intermetallics” means a body-centered cubic (BCC) intermetallic of the base metal M and Al. “Y-type intermetallics” means an intermetallic of yttrium and the base metal M or other metallic elements. As is understood, typically the γ-M solid solution, a β-MAl intermetallic phase, and Y-type intermetallics will result from the heat treatment of an MCrAIY material under specific temperature, time, and atmospheric requirements.
Within this disclosure, "YAG" means a Yttrium-Aluminum Garnet having the chemical structure $\text{YAlO}_3$; "YAP" means a Yttrium-Aluminum Perovskite having the chemical structure $\text{YAl}_2$ and "Ytria" means a Yttrium-oxide having the chemical structure $\text{Y}_2\text{O}_3$.

Within this disclosure, a "substantial absence" of Ytria, YAG, and YAP phases within a Y-Al₂O₃ layer means that cathodoluminescence of the Y-Al₂O₃ layer generates a CL emission spectra where absorption peaks corresponding to Ytria, YAG, and YAP wavelengths are undetectable above background. Similarly, a "substantial absence" of YAG and YAP phases within a MCRAIY layer means that cathodoluminescence of the MCRAIY layer generates a CL emission spectra where absorption peaks corresponding to YAG and YAP wavelengths are undetectable above background.

The disclosure further provides for a process for producing the bond coated article disclosed comprised briefly of depositing an MCRAIY material on a substrate, preparing a Y₂O₃ paste comprised of a halide activator, and heat treating the article in a non-oxidizing atmosphere. The process generates the MCRAIY layer and the Y-Al₂O₃ layer disclosed by blocking oxygen diffusion into the MCRAIY bulk during heat treatment and mitigating Ytrium diffusion toward the surface, thereby avoiding significant variation in the intended Y-distribution and the Ytrium reservoir.

Fig. 1 illustrates an embodiment of a bond coat having MCRAIY layer 101 in contact with substrate 103 at substrate surface 105, and further in contact with Y-Al₂O₃ layer 102 at MCRAIY upper surface 106, where substrate surface 105 is a surface of substrate 103 and MCRAIY upper surface is a surface of MCRAIY layer 101.

At Fig. 1, Y-Al₂O₃ layer 102 is comprised of Yttrium atoms and Al₂O₃, where the Yttrium atoms are coordinated with oxygen atoms comprising the Al₂O₃ lattice. Generally and without being bound by theory, Y-Al₂O₃ layer 102 is comprised of equiaxed grains of Al₂O₃ where the Al₂O₃ grain boundaries are enriched with Ytrium at grain-boundary cation sites. Typically the grain-boundary enrichment is reflected by an enrichment factor of at least 100, where the enrichment factor is the ratio of Ytrium concentration at grain boundaries to that within some statistically significant population of grains, with an average grain-boundary cation coverage of typically between 6 and 10% See, e.g., Thompson et al., "Dopant Distributions in Rare-Earth-Doped Alumina," J. Am. Ceram. Soc., 80 [2] (1997). The Ytrium enrichment along the grain boundary provides significant benefit in terms of oxygen diffusion within Y-Al₂O₃ layer 102, as is understood. In some cases, Ytrium enrichment along the grain boundaries of Al₂O₃ has generated diffusivities up to 10 times lower than that of pristine grain boundaries. See, e.g., Nakagawa et al., "Ytrium doping effect on oxygen grain boundary diffusion in a-Al₂O₃," Acta Materialia 55 (2007).

Additionally, Y-Al₂O₃ layer 102 has a substantial absence of Ytria, YAG, and YAP phases, as opposed to the typical upper layers generated through the vacuum heat treatment of MCRAIY materials. In typical vacuum heat treatments, where residual oxygen partial pressures on the order of $10^{-5}$ mbar are experienced, the formation of Yttria and mixed Y-Al oxide compounds is expected. These compounds result from the high oxygen affinity of Ytrium driving a Ytrium diffusion from within the bulk of the MCRAIY material, which modifies the originally intended Y-distribution in the heat-treated MCRAIY bondcoat. Additionally, Ytria and mixed Y-Al oxide compounds, particularly large YAG particles, are linked to increased scale spallation due to stress concentration and thermal expansion mismatch. See, e.g., Pint, "Optimization of Reactive-Element Additions to Improve Oxidation Performance of Alumina-Forming Alloys," J. Am. Ceram. Soc., 86 [4] (2003). The absence of Ytria, YAG, and YAP phases within Y-Al₂O₃ layer 102 is thus a configuration which is both difficult to achieve and advantageous in operational service.

The Y-Al₂O₃ layer may be a continuous or discontinuous layer. For example, FIG. 2 illustrates MCRAIY layer 201 in contact with substrate 203 at substrate surface 205, and further in contact with Y-Al₂O₃ layer 202 at MCRAIY upper surface 206, where Y-Al₂O₃ layer 202 is a discontinuous layer comprised of Y-Al₂O₃ regions such as Y-Al₂O₃ region 204. When the Y-Al₂O₃ layer is comprised of regions such as Y-Al₂O₃ region 204, the individual Y-Al₂O₃ regions have the same properties as those described for the Y-Al₂O₃ layer, such as Y-Al₂O₃ layer 102. As such, whether the Y-Al₂O₃ layer is a continuous or discontinuous layer is not a limitation of this disclosure. Within this disclosure, it is only necessary that the Y-Al₂O₃ layer whether continuous or discontinuous is in contact with the MCRAIY upper surface, and that when the MCRAIY layer is in contact with a substrate surface, that the Y-Al₂O₃ layer is separated from the substrate surface by at least some portion of the MCRAIY layer.

At FIG. 1, MCRAIY layer 101 is comprised of Ytrium and Aluminum, and further comprised of at least 50 wt. % of a metal M, at least 10 wt. % Cr, and at least 7 wt. % Al, where the metal M is Ni, Co, Fe, or combinations thereof, and comprised of phases including a γ-M solid solution, a δ-M Al intermetallic phase, and Y-type intermetallics. Depending on the exact chemical composition of MCRAIY layer 101, additional phases may also be present. Generally, the structure of MCRAIY layer 101 is comprised of distinct γ-M solid solution and δ-M Al intermetallic phases, with Y-type intermetallics between the phases. In an embodiment, an MCRAIY material utilized to form MCRAIY layer 101 has an MCRAIY composition comprised of from about 15 to about 25 wt. % chromium, from about 7 to about 15 wt. % aluminum, from about 0.05 to about 0.5 wt. % yttrium, and at least 50 wt. % of the base metal M, where the wt. % values are based on the total weight of the composition.

Additionally, MCRAIY layer 101 has a substantial absence of YAG and YAP phases, as opposed to typical MCRAIY bond coats generated through the vacuum heat treatment of MCRAIY materials. Generally, residual oxygen partial pressure in typical vacuum chambers is on the order of $10^{-5}$ mbar, resulting in the formation of mixed Y-Al oxide compounds. Depending on the Ytrium content of the MCRAIY material and the oxygen partial pressure employed, Y-Al oxide compounds can additionally be expected within the bulk of the MCRAIY bond coat layer, along with, in some cases, a generally continuous layer of yttria and significant Ytrium diffusion toward the surface. See, e.g., Gil et al., "Y-rich oxide distribution in plasma sprayed MCRAIY-coatings studied by SEM with a cathodoluminescence detector and Raman spectroscopy," Surface & Coatings Technology 204 (2009); and see Subanovic et al., "Effect of manufacturing related parameters on oxidation properties of MCRAIY-bondcoats," Materials and Corrosion 59 (2008). This generated Y-oxide distribution modifies the Y-distribution within the MCRAIY bulk and has a significant effect on the growth rate and adherence of the alumina scale and lifetime of the bond coat. Additionally, because significant variations in the Y-distribution and the reservoir of metallic Y in MCRAIY coatings can be caused by only minor variations in the processing parameters, the alumina scale growth rate and adherence may be different for nominally the same MCRAIY bondcoats, negatively impacting the reproducibility of bond coat lifetimes. See, e.g.,
Toscano et al., "Parameters affecting TGO growth rate and the lifetime of TBC systems with McRAIY-bondcoats," *Materials and Corrosion* 59 (2008), among others. Thus, the substantial absence of YAG and YAP phases within the McRAIY layer 101 provides a more uniform and predictable Y-distribution and significantly mitigates issues associated with Y-oxide formation and altered Y-distribution profiles.

When McRAIY layer 101 is a cast layer, it is expected that McRAIY layer 101 will additionally have a substantial absence of Yttria in addition to the absence of YAG and YAP phases. However, depending on the method of fabrication, some Yttria formed during application may be unavoidably present. See e.g., Gudmundsson et al., "Yttrium oxides in Vacuum-plasma Sprayed CoNiCrAlY Coatings," *Thin Solid Films*, 173 (1989), among others.

It is known that Yttria, YAG, and YAP exhibit significant cathodoluminescence and may be utilized to determine the morphology and distribution of Y2O3 and Y—Al mixed oxide phases within McRAIY coatings. See Gil et al. and see Subanovic et al., among others. Correspondingly, as used herein and above, a "substantial absence" of Yttria, YAG, and YAP phases within Y—Al2O3 layer 102 means that cathodoluminescence of some portion of Y—Al2O3 layer 102 generates a CL emission spectra where absorption peaks corresponding to Yttria, YAG, and YAP wavelengths are undetectable above the background. Similarly, a "substantial absence" of YAG and YAP phases within the McRAIY layer 101 means that cathodoluminescence of some portion of the McRAIY layer 101 generates a CL emission spectra where absorption peaks corresponding to YAG and YAP wavelengths are undetectable above the background.

As stated, the McRAIY layer 101 is comprised of a γ-PrM solid solution, a β-MAI intermetallic phase, and γ-type intermetallics. As defined, a "γ-type intermetallic" as used herein means an intermetallic compound consisting of Yttrium and at least one other metal. For example, when the McRAIY layer 101 derives from a source material composition where the base metal M is Nickel and Cobalt, the McRAIY layer 101 may be comprised of Ni2Y, Co2Y, and Cr2Y, among others, as γ-type intermetallics. These intermetallics define a Yttrium atomic concentration within the McRAIY layer 101 which is relatively stable around the original Yttrium atomic concentration of the McRAIY source material utilized to generate the McRAIY layer. For example, when the McRAIY source material has an McRAIY composition comprised of 0.1 wt. % Yttrium, and McRAIY layer 101 comprised of γ-M solid solution, a β-MAI intermetallic phase, and γ-type intermetallics results from heat treatment of the McRAIY source material, the resulting Y-type intermetallics define a Yttrium atomic concentration within the McRAIY layer 101 approximately equivalent 0.1 wt. % Yttrium. Also, McRAIY layers where even low oxygen partial pressures during heat treatment are sufficient to tie up a significant portion of the McRAIY source material’s Yttrium in Y—Al oxides within the McRAIY bulk. Additionally, as will be discussed infra, the diffusion of Yttrium toward the surface is mitigated during vacuum heat treatment, resulting in a relatively homogenous Yttrium distribution within the McRAIY layer 101.

Maintaining a significant majority of the Yttrium as a Y-type intermetallic has distinct advantage over McRAIY layers where a significant portion of the Yttrium component may be tied up in Y—Al oxide inclusions, effectively removing that Yttrium from the available Yttrium reservoir of the McRAIY layer. There is strong indication that an important life time governing factor of McRAIY coatings is the Yttrium incorporation into the alumina based Thermal Grown Oxide (TGO) formed during service, which correspondingly generates a decrease of the yttrium concentration in the coating over a component lifetime. If the Yttrium concentration is decreased below a critical level, its positive effect on TGO adherence is lost, resulting in TGO spallation. See e.g., Toscano et al., "Parameters affecting TGO growth rate and the lifetime of TBC systems with McRAIY-bondcoats," *Materials and Corrosion* 59 (2008). Thus, within the McRAIY layer of this disclosure, maintaining a large majority of the Yttrium component in the form of Y-type intermetallics with a substantial absence of Y—Al oxides acts to maximize the Yttrium reservoir of the material, delaying spallation of thermally grown oxides during subsequent service.

In an embodiment, the Yttrium within a McRAIY layer such as McRAIY layer 101 defines a Yttrium component, and the Y-type intermetallics within the McRAIY layer are comprised of at least 90 wt. % of the Yttrium within the Yttrium component. Stated differently, 90 wt. % of the Yttrium in the McRAIY layer is in the form of a γ-type intermetallic.

As indicated at Fig. 1, McRAIY layer 101 may be further in contact with substrate surface 105 of substrate 103. In an embodiment, substrate 103 is nickel-base alloy, and the base metal M comprising the McRAIY layer 101 is Ni, Co, or Ni and Co. Additionally, Y—Al2O3 layer 102 may be further in contact with the substrate 107. In an embodiment, the substrate 107 is comprised of yttria stabilized zirconia. In a particular embodiment, McRAIY layer 101 and Y—Al2O3 layer 102 are fabricated by a process of depositing an McRAIY material on a substrate, preparing a Y2O3 paste comprised of a halide activator, and heat treating the article in a non-oxidizing atmosphere to generate the McRAIY layer and the Y—Al2O3 layer, as follows:

Depositing the McRAIY Material on the Substrate:

As earlier defined, an McRAIY material is a material having a material composition comprised of a base metal M, chromium, aluminum, and yttrium. The base metal M is typically Iron, Nickel, Cobalt, or a combination of Nickel and Cobalt. Generally, the McRAIY material has an McRAIY composition comprised of from about 15 to about 25 weight percent (wt. %) chromium, from about 7 to about 15 wt. % aluminum, from about 0.05 to about 0.5 wt. % yttrium, and greater than about 50 wt. % of the base metal M, where the wt. % values are based on the total weight of the composition. In an embodiment, the McRAIY material has an McRAIY composition comprised of 22 wt. % Cr, 10 wt. % Al, 1 wt. % Y, balance Ni. In another embodiment, the McRAIY material has an McRAIY composition of 32 wt. % Ni, 21 wt. % Cr, 8 wt. % Al, 0.5 wt. % Y, balance Co.

The McRAIY material composition described can be manufactured as a powder for use in depositions using, for example, a spraying technique. The material composition including all elemental constituents may be prepared with powders generated by conventional powder processing methods, such as inert gas atomization from ingots. Alternatively, powder blends may be prepared by mixing separate powders of individual elements or alloys. In a final powder composition prepared in this manner the weight percentage of each elemental constituent corresponds to the ranges earlier provided. A preferred diameter for the metallic powder particles, regardless how formed, is between about 5 to about 50 microns.

The McRAIY material is deposited as a coating layer on a substrate surface, such as substrate surface 335 of substrate 333 at Fig. 3. The McRAIY material 331 is deposited using conventional methods, such as low pressure plasma spray (LPPS), electron beam physical vapor deposition (EBPVD), High Velocity Oxygen Fuel (HVOF) spray, or other methods.
known in the art for deposition of an MCRAIY material onto a substrate surface. See e.g., Pawlowski, *The Science and Engineering of Thermal Spray Coatings* (2nd Ed. 2008). In an embodiment, the MCRAIY material 331 is deposited on the substrate surface to a thickness of about 20 microns. In another embodiment where the base metal M of the MCRAIY material 331 is Nickel or Cobalt, the substrate is comprised of a nickel-base alloy. Deposition of the MCRAIY material onto substrate surface 335 of substrate 333 generates an MCRAIY material surface 336, where the MCRAIY material surface 336 is a surface of the MCRAIY material 331 separated from substrate surface 335 by some portion of MCRAIY material 331.

In an embodiment, the MCRAIY material has an MCRAIY composition comprised of 22 wt. % Cr, 10 wt. % Al, 1.0 wt. % Y, balance Ni, or comprised of 32 wt. % Ni, 21 wt. % Cr, 8 wt. % Al, 0.5 wt. % Y, balance Co, and the MCRAIY material is deposited by atmospheric plasma spray (APS) or high velocity oxygen fuel (HVOF) on a substrate comprised of an advanced Ni-based single crystal alloy, such as RENE 85 developed by General Electric Company, PW1484 developed by Pratt & Whitney, RR2000 developed by Rolls-Royce, or CMSX-4 developed by Cannon Muskegon Corporation, and the equivalents.

Preparing a Y$_2$O$_3$ Paste:

The Y$_2$O$_3$ paste is comprised of Y$_2$O$_3$ and a halide activator, and may be further comprised of inert filler and inert transport fluid. In an embodiment, the Y$_2$O$_3$ comprising the Y$_2$O$_3$ paste is at least 10 wt. % of the combined weight of the Y$_2$O$_3$, halide activator, and inert filler, and the halide activator is at least about 0.1 wt. % of the combined weight of the Y$_2$O$_3$ and the halide activator. Y$_2$O$_3$ is commercially available as a powder with typical purities of 99.5 wt. % to 99.99 wt. %. Although any particle size may be employed, it has been found advantageous to use particles of relatively fine size. Preferably, the Y$_2$O$_3$ is relatively fine for ease in suspending in a paste or slurry. Generally, Y$_2$O$_3$ particle size is less than 200 microns, preferably less than 45 microns, and more preferably less than 10 microns.

The halide activator serves to react with the Y$_2$O$_3$ powder during a high temperature coating process to produce yttrium containing vapors which are carried to the MCRAIY upper surface. The halide activator may be selected from any of the activators known for use in the pack cementation technique and suitable for the production of yttrium containing vapors when placed in the presence of Y$_2$O$_3$ at sufficient temperature. Suitable halide activators may be selected from any of the activators known for this purpose and combinations thereof and equivalents. Typically the halide activator includes one or more halide salts. Suitable halide activators include AlF$_3$, AlCl$_3$, NH$_4$F, NH$_4$Cl, NaF, NaCl, KF, and KCl, among others.

In an embodiment, the halide activator is present in an amount of at least about 0.1 wt. % of the combined weight of the Y$_2$O$_3$ and the halide activator. In an embodiment, the Y$_2$O$_3$ paste is comprised of 0.5 g NaCl per 150 g Y$_2$O$_3$.

The inert filler is a material which is not reduced by yttrium-containing vapors and which prevents the sintering of Y$_2$O$_3$. Generally, the inert filler may comprise 10 wt. % to 80 wt. % of the Y$_2$O$_3$ paste. Fillers are known in the art that inhibit sintering of Y$_2$O$_3$ and include alumina, thoria, calcia, zirconia and other stable and inert refractory oxides and mixtures thereof. The inert filler may be added in the same particle size range as the Y$_2$O$_3$, with typical particle size less than 200 microns, preferably less than 45 microns, and more preferably less than 10 microns.

The Y$_2$O$_3$ halide activator and optionally, inert filler, are combined and thoroughly mixed as required to make the Y$_2$O$_3$ paste composition. An inert transport fluid such as water may be added, generally in an amount of about 30 wt.% to 40 wt.% of the Y$_2$O$_3$ paste. In an embodiment, the Y$_2$O$_3$ paste is comprised of 0.5 g NaCl and 150 g Y$_2$O$_3$ per 100 cc of water. This is stirred until it has a consistency of about milk or cream. Frequent stirring or continuous stirring during application provides the best coating.

Applying the Y$_2$O$_3$ Paste and Heating the Paste Covered Article:

The Y$_2$O$_3$ paste is applied to the MCRAIY material surface by any convenient, cost effective manner. Dipping, brushing and spraying are all effective. In an embodiment, the Y$_2$O$_3$ paste is applied to the MCRAIY material surface in a layer less than about 1 micron thick. FIG. 3 illustrates Y$_2$O$_3$ paste 332 applied to MCRAIY material surface 336. Application of Y$_2$O$_3$ paste 332 to MCRAIY material surface 336 generates a paste covered article, where the paste covered article is comprised of substrate 333, MCRAIY material 331, and Y$_2$O$_3$ paste 332, where MCRAIY material 331 is in contact with substrate 333 at substrate surface 335 and further in contact with Y$_2$O$_3$ paste 332 at MCRAIY material surface 336, and where Y$_2$O$_3$ paste 332 is separated from substrate 333 by at least some portion of MCRAIY material 331, as illustrated at FIG. 3. In an embodiment, a topcoat material such as yttria stabilized zirconia is then applied to the surface of the Y$_2$O$_3$ layer.

The paste covered article is then heated in a non-oxidizing atmosphere at a temperature of from about 400°C to about 1300°C for a sufficient period of time sufficient to generate the MCRAIY layer and the Y—Al$_2$O$_3$ layer, where the MCRAIY layer and the Y—Al$_2$O$_3$ layer have properties as described. In an embodiment, the paste covered article is heated at a temperature of about 900°C for a period of about 2 hours. A “non-oxidizing atmosphere” as used in this disclosure means an atmosphere having either a total pressure or partial pressure of oxygen less than about 10$^{-5}$ mbar.

Following the heating period, any excess remaining Y$_2$O$_3$ paste may be removed from the heat treated article, generating a bond coated article.

The method as described above may be utilized for the production of the bond coated article comprised of the Y—Al$_2$O$_3$ layer and the MCRAIY layer as described. Without being bound by theory, it is believed that utilization of the Y$_2$O$_3$ paste in the non-oxidizing atmosphere as described acts to severely mitigate the diffusion of any residual oxygen existing during the heat treatment prescribed. This residual oxygen is typically present in vacuum heat treatment furnaces, which generally exhibit oxygen pressures on the order of 10$^{-7}$ mbar during operation. As is understood, Yttrium has the highest oxygen affinity in typical MCRAIY materials, and Yttria is generally the first oxide to form during early oxidation stages. The low oxygen pressure exhibited by standard vacuum heat furnaces is sufficient to generate a strong diffusion of Yttrium within the MCRAIY material toward the surface and subsequent oxidation, as well as the formation of YAG and YAP phases within the MCRAIY bulk. The method as described above allows the formation of a bond coated article comprised of the Y—Al$_2$O$_3$ layer and the MCRAIY layer as described by blocking oxygen diffusion into the MCRAIY bulk during heat treatment, resulting in a Y—Al$_2$O$_3$ layer comprised of equiaxed grains of Al$_2$O$_3$ enriched with Yttrium at grain-boundary cation sites and having a substantial absence of Yttria, YAG, and YAP phases, and an MCRAIY layer in contact with the Y—Al$_2$O$_3$ layer, where the MCRAIY layer is comprised of γ-M solid solution, β-MAl intermetallics, and Y-type intermetallics with a substantial absence of YAG and YAP phases. The produced material thus avoids
significant variation in the intended Y-distribution and the reservoir of metallic Y in MCRAIY coatings, and mitigates the negative impacts to bond coat lifetimes.

It is to be understood that the above-described arrangements are only illustrative of the application of the principles of the present invention and it is not intended to be exhaustive or limit the invention to the precise form disclosed. Numerous modifications and alternative arrangements may be devised by those skilled in the art in light of the above teachings without departing from the spirit and scope of the present invention. It is intended that the scope of the invention be defined by the claims appended hereto.

In addition, the previously described versions of the present invention have many advantages, including but not limited to those described above. However, the invention does not require that all advantages and aspects be incorporated into every embodiment of the present invention.

All publications and patent documents cited in this application are incorporated by reference in their entirety for all purposes to the same extent as if each individual publication or patent document were so individually denoted.

What is claimed is:

1. A bond coat comprised of:
   an MCRAIY layer, where the MCRAIY layer has an MCRAIY composition comprised of yttrium, aluminum, chromium, and at least 50 wt. % of a base metal M, where the base metal M is Ni, Co, or Fe, and where the MCRAIY layer is comprised of γ-M solid solution, β-MAI intermetallic, and Y-type intermetallics, and where the MCRAIY layer has a substantial absence of Yttrium-Aluminum Garnet and Yttrium-Aluminum Perovskite, such that a cathodoluminescence of the MCRAIY layer generates a MCRAIY CL emission spectra where absorption peaks corresponding to Yttrium-Aluminum Garnet and Yttrium-Aluminum Perovskite are undetectable above background, and where the MCRAIY layer has an MCRAIY upper surface, where the MCRAIY upper surface is a surface of the MCRAIY layer; and
   a Y—Al_2O_3 layer, where the Y—Al_2O_3 layer is in contact with the MCRAIY upper surface, where the Y—Al_2O_3 layer comprises of yttrium atoms and Al_2O_3, where the yttrium atoms are coordinated with oxygen atoms comprising the Al_2O_3, and where the Y—Al_2O_3 layer has a substantial absence of Yttrium-Aluminum Garnet, Yttrium-Aluminum Perovskite, and yttria, such that a cathodoluminescence of the Y—Al_2O_3 layer generates a Y—Al_2O_3 CL emission spectra where absorption peaks corresponding to Yttrium-Aluminum Garnet, Yttrium-Aluminum Perovskite, and yttria wavelengths are undetectable above background.

2. The bond coat of claim 1 where the MCRAIY composition is comprised of from about 15 to about 25 wt. % chromium, from about 10 to about 15 wt. % aluminum, and from about 0.05 to about 1.5 wt. % yttrium.

3. The bond coat of claim 2 where the MCRAIY layer has a weight percent of yttrium within the MCRAIY layer, and where the Y-type intermetallics of the MCRAIY layer comprise at least 90% of the weight percent of yttrium within the MCRAIY layer.

4. The bond coat of claim 3 further comprised of a substrate having a substrate surface, where the MCRAIY layer is in contact with the substrate surface, such that the MCRAIY layer is between the substrate and the Y—Al_2O_3 layer.

5. The bond coat of claim 4 further comprised of a topcoat in contact with the Y—Al_2O_3 layer, such that the Y—Al_2O_3 layer is between the topcoat and the MCRAIY layer.

6. The bond coat of claim 4 where the MCRAIY composition is comprised of less than about 0.15 wt. % yttrium.

7. The bond coat of claim 6 where the substrate is comprised of a nickel-base alloy, and where the metal base M is Ni or Co.

8. The bond coat of claim 7 where the MCRAIY layer is less than about 20 microns thick and the Y—Al_2O_3 layer is less than about 1 micron thick.

9. The bond coat of claim 8 further comprised of a topcoat in contact with the Y—Al_2O_3 layer, such that the Y—Al_2O_3 layer is between the topcoat and the MCRAIY layer.

10. The bond coat of claim 9 where the topcoat is comprised of yttria stabilized zirconia.

11. The bond coat of claim 2 where the substrate is comprised of a nickel-base alloy, and where the metal base M is Ni, Co, or Ni and Co, and where the MCRAIY composition is comprised of less than about 0.15 wt. % yttrium, and where the MCRAIY layer is less than about 20 microns thick and the Y—Al_2O_3 layer is less than about 1 micron thick.

12. The bond coat of claim 11 further comprised of a topcoat in contact with the Y—Al_2O_3 layer, such that the Y—Al_2O_3 layer is between the topcoat and the MCRAIY layer.

13. A bond coat comprised of:
   an MCRAIY layer, where the MCRAIY layer has an MCRAIY composition comprised of from about 15 to about 25 wt. % chromium, from about 10 to about 15 wt. % aluminum, from about 0.05 to about 0.5 wt. % yttrium, and at least 50 wt. % of a base metal M, where the base metal M is Ni, Co, or Fe, and where the MCRAIY layer is comprised of γ-M solid solution, β-MAI intermetallic, and Y-type intermetallics, and where the MCRAIY layer has a substantial absence of Yttrium-Aluminum Garnet and Yttrium-Aluminum Perovskite, such that a cathodoluminescence of the MCRAIY layer generates a MCRAIY CL emission spectra where absorption peaks corresponding to Yttrium-Aluminum Garnet and Yttrium-Aluminum Perovskite are undetectable above background, and where the MCRAIY layer has a weight percent of Yttrium within the MCRAIY layer, where the Y-type intermetallics of the MCRAIY layer comprise at least 90% of the weight percent of yttrium within the MCRAIY layer, and where the MCRAIY layer has an MCRAIY upper surface, where the MCRAIY upper surface is a surface of the MCRAIY layer; and
   a Y—Al_2O_3 layer, where the Y—Al_2O_3 layer is in contact with the MCRAIY upper surface, where the Y—Al_2O_3 layer comprises of yttrium atoms and Al_2O_3, where the yttrium atoms are coordinated with oxygen atoms comprising the Al_2O_3, and where the Y—Al_2O_3 layer has a substantial absence of Yttrium-Aluminum Garnet, Yttrium-Aluminum Perovskite, and yttria, such that a cathodoluminescence of the Y—Al_2O_3 layer generates a Y—Al_2O_3 CL emission spectra where absorption peaks corresponding to Yttrium-Aluminum Garnet, Yttrium-Aluminum Perovskite, and yttria wavelengths are undetectable above background.

14. The bond coat of claim 13 where the metal base M is Ni or Co.

15. The bond coat of claim 14 where the MCRAIY composition is comprised of less than about 0.15 wt. % Yttrium.

16. The bond coat of claim 15 further comprised of a substrate having a substrate surface, where the MCRAIY layer is in contact with the substrate surface, such that the MCRAIY layer is between the substrate and the Y—Al_2O_3 layer, and where the substrate is comprised of a nickel-base alloy.
17. The bond coat of claim 16 where the MCrAlY layer is less than about 20 microns thick and the Y—Al₂O₃ layer is less than about 1 micron thick.

18. The bond coat of claim 17 further comprised of a topcoat in contact with the Y—Al₂O₃ layer, such that the Y—Al₂O₃ layer is between the topcoat and the MCrAlY layer, and where the topcoat is comprised of yttria stabilized zirconia.

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